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EFFECT OF LOW ILLUMINATION DURING OXIDATION-REDUCTION CYCLES UP--ETC(U)

JUL 82 F BARZ, J G GORDON, M R PHILPOTT

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Effect of <sup>Low</sup>~~Low~~

by

F. Barz, J. G. Gordon, M. R. Philpott and M. J. Weaver

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The intensity of surface-enhanced Raman scattering from thiocyanate and chloride adsorbed at silver electrodes is shown to depend critically on whether the electrode is illuminated during the oxidation-reduction cycle (ORC) used to pretreat the electrode. The nature and magnitude of the photoeffect is dependent upon the type of surface vibrational mode, the adsorbate, and the wavelength of the irradiation during the ORC.		

In this note, we report measurements to show clearly that the intensity of surface enhanced Raman scattering (SERS) from thiocyanate and chloride anions adsorbed on silver electrodes depends critically on the intensity of the laser beam illuminating the electrode during the oxidation-reduction cycle (ORC). It is well-established that intense SERS spectra are readily obtained from silver, copper and gold electrodes immersed in aqueous electrolytes after the metal is "roughened" by means of an ORC.<sup>1</sup> This involves either an anodic-cathodic potential sweep or a step to and then from a potential where the electrode undergoes oxidation, using halide ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) or pseudohalide (e.g.,  $\text{SCN}^-$ ,  $\text{N}_3^-$ ,  $\text{CN}^-$ ), supporting electrolytes that form sparingly soluble complexes with  $\text{Ag(I)}$ . The experiments described here form part of an ongoing investigation of the SERS of these anions at silver, with a view towards comparing the Raman characteristics of such structurally simple electrochemical adsorbates with the thermodynamics of their adsorption obtained from differential capacitance measurements. In the course of these studies, we have noted for several systems a striking influence of illumination of the electrode surface during the ORC upon the resulting Raman intensities. Some main features of this effect that have been studied so far are reported in this communication, along with its implications for the understanding of the mechanisms responsible for SERS with such simple inorganic systems.

A variety of laser induced effects at the electrode-electrolyte interface are known or suspected.<sup>1-7</sup> At very high laser powers ( $10^4 \text{ Wcm}^{-2}$ ) the double layer is disrupted and effects like greatly increased plating are observed.<sup>6</sup> At the much lower power levels used in SERS experiments, it has been known for some time that powers greater than several hundred mW cause selective decreases in certain modes of the adsorbates. Since many silver salts undergo photolysis, it is not surprising to find an effect due to visible laser light for adsorbates on silver electrodes. What is surprising, however, is the fact that heretofore the

effect during the ORC has gone unrecognized. After the present work was completed, we learned of a similar effort by Macomber et al.<sup>8</sup> who also observed a difference in SERS spectra taken after ORCs performed with the laser on or blocked from the electrode.

Figure 1 shows Raman spectra spanning the 100-500  $\text{cm}^{-1}$  and 2000-2200  $\text{cm}^{-1}$  regions for thiocyanate ions ( $\text{SCN}^-$ ) adsorbed on silver at -100 mV (versus Ag/AgCl). The spectra shown are actual single scans from a Spex model 14018 double monochromator. The electrolyte was 0.1M NaCl+0.01M NaSCN, and the electrode pretreatment entailed mechanical polishing with 0.3  $\mu\text{m}$  alumina, rapid rinsing with distilled water, immersing in the electrolyte, and stepping from -100 mV to +250 mV and return to -100 mV after 20  $\text{mC cm}^{-2}$  of anodic charge had passed. Further details concerning the apparatus and experimental procedures are given in Refs. 7 and 9 respectively.

Curve A in Fig. 1 was recorded before the ORC, and curve B was recorded after an ORC was performed without allowing the laser to illuminate the silver surface. For convenience, we call the latter type a "dark ORC," to distinguish them from an oxidation-reduction cycle performed with the laser irradiating the sample with up to several hundred mW of power. Notice that in trace B, there are discernible but weak peaks at 210  $\text{cm}^{-1}$  and 2115  $\text{cm}^{-1}$ , associated with metal-ligand ( $\nu_{\text{ML}}$ , probably the Ag-S stretching mode) and C-N stretching ( $\nu_{\text{CN}}$ ) modes, whereas a larger intensity is found for the usually weak 450  $\text{cm}^{-1}$  peak associated with the N-C-S angle bending mode ( $\delta_{\text{SCN}}$ ).<sup>9-11</sup> Trace C in Fig. 1 was obtained under the same conditions as B, except that the laser used to record the Raman spectra (wavelength  $\lambda_{\text{L}} = 530.9 \text{ nm}$ , incident power  $P_{\text{L}} = 200 \text{ mW}$ , p-polarized and line focussed to an area approximately  $1 \times 5 \text{ mm}$  at the sample) was also illuminating the metal surface during the ORC. The intensities of both the  $\nu_{\text{ML}}$  and  $\nu_{\text{CN}}$  bands are

substantially increased compared to trace B, along with a noticeable increase in the level of the continuum background. Note that in contrast, the  $\delta_{\text{NCS}}$  mode remains unaffected by the laser illumination during the ORC (see Fig. 1).

In a separate set of experiments, a series of identical double potential step ORC's were performed, first with the laser beam blocked from the electrode (dark ORC) and then with the laser continuously irradiating the electrode. Immediately following each ORC, the entire  $\nu_{\text{CN}}$  band from 1848 to 2330  $\text{cm}^{-1}$  was recorded using a Spex model 1877 spectrograph equipped with an optical multichannel analyzer (OMA). Continuous laser irradiation results in a large increase in Raman intensity for the  $\nu_{\text{CN}}$  band. In Fig. 2A, we show a set of spectra (1,2,...,5; note that all OMA spectra have high frequency on the left) taken immediately after each dark ORC. To obtain these spectra, the laser illuminated the electrode only long enough to record the spectrum (2 s). The electrode potential was -100 mV and the laser parameters were the same as for the Fig. 1 experiments. The corresponding five spectra in Fig. 2B were again recorded under identical conditions to those in Fig. 2A (e.g., starting with a freshly polished electrode), but with the laser illuminating the surface during each ORC. Like the example shown in Fig. 1, the  $\nu_{\text{CN}}$  signal intensities in Fig. 2B are uniformly higher than those resulting from dark ORCs. However, the relative signal enhancement as a result of laser illumination during the ORC rapidly diminishes with increasing number of successive oxidation-reduction cycles.

We repeated the foregoing series using a red line of the krypton laser  $\lambda_{\text{L}} = 647.1 \text{ nm}$  to illuminate the electrode during the ORC's and to record Raman spectra. In contrast to the results with green light, it was found that the enhancement of  $\nu_{\text{CN}}$  signal intensity resulting from 647.1 nm irradiation during the ORC's was barely discernible even for laser powers as

high as 600 mW. These results clearly show that the photoeffect is sensitive to the wavelength of the incident light.

All the measurements described above refer to a mixed electrolyte 0.1M NaCl+0.01M NaSCN; although almost identical spectra were obtained using 0.1M NaClO<sub>4</sub> in place of 0.1M NaCl. We also performed similar experiments with silver electrodes immersed in 0.1M NaCl. Trace A in Fig. 3 is a spectrum for the region 100-350 cm<sup>-1</sup> for silver at -100 mV in 0.1M NaCl, recorded following a double potential step "dark ORC" in which 20 mC cm<sup>-2</sup> of anodic charge was passed ( $\lambda_L$ =530.9 nm,  $P_L$ =200 mW, p-polarized). A discernible band at 240 cm<sup>-1</sup> was obtained, although it was weak compared to the sharply falling background arising from stray light and Rayleigh scattering. This band is due to a metal surface-chloride stretching vibration ( $\nu_{MCl}$ ).<sup>11-13</sup> Trace B is the spectrum obtained for the same conditions but with the laser illuminating the electrode during the ORC. As before, there is a marked enhancement of the signal intensity arising from photoeffect during the ORC along with a large increase in the intensity of the continuum background. Figure 4 shows the corresponding pair of spectra under the same conditions, but using 647.1 nm radiation. In contrast to the behavior of the thiocyanate SERS spectra above, the  $\nu_{MCl}$  intensity is strikingly increased by laser illumination during the ORC, so much so that the signal intensity relative to the continuum background (Fig. 4) is greater than that observed using 530.9 nm illumination (Fig. 3). Wetzal et al.<sup>12</sup> have recently reported that laser excitation at 647.1 or 676.4 nm yielded easily observable  $\nu_{MCl}$  signals for silver in 0.1M NaCl, whereas no detectable SERS spectra were obtained using 514 nm light under the same conditions.

Extensive laser power and wavelength dependence studies have been made for silver electrodes in contact with 0.1M NaCl.<sup>14</sup> No threshold effect in laser power in the range 0.1 to 500 mW was observed. A difference in light and dark ORCs was induced using focussed light from a tungsten lamp. Above 500 mW, the effect appears to saturate. Sensitivity to the wavelength of the laser was confirmed by an experiment in which a second laser was used solely to illuminate the electrode. Raman scattering observed in this two laser experiment indicated that the effect does not depend monotonically on the wavelength of the second laser, but exhibited a maximum in the yellow.<sup>14</sup>

The results described above and so graphically illustrated in Figs. 1-4 indicate that laser illumination during the electrochemical roughening process can have a profound influence upon the intensity of the resulting SERS spectra, to an extent which depends upon the nature of the adsorbate, the wavelength of the incident radiation, and also the type of vibrational mode that is surface enhanced.

Two aspects of these results are worthy of further comment at this stage. First, we note the fundamentally different behavior of the angle bending mode  $\delta_{\text{SCN}}$  of adsorbed thiocyanate compared to both  $\nu_{\text{ML}}$  and  $\nu_{\text{CN}}$  toward laser illumination. This, together with information compiled elsewhere,<sup>9</sup> strongly suggests that the absorption sites responsible for the observed bending mode are structurally distinct and possibly also associated with a different orientation of the adsorbed thiocyanate ions, from those giving rise to the strong  $\nu_{\text{ML}}$  and  $\nu_{\text{CN}}$  Raman bands.<sup>15</sup> Second, we comment on the mechanism whereby different enhancements follow ORC's performed with the laser off and on. A simple explanation assumes that the effect is due to a more facile creation of silver nuclei that are rich in SERS active sites. If the electrode is illuminated during the ORC, then photon absorption promotes



the creation of numerous silver nuclei which grow during the cathodic return step and develop surfaces that adsorb ligands to the SERS active sites, or have centers that in the presence of ligands convert to such sites. Thus, the effect is somewhat analogous to latent image formation in silver halide grains exposed to visible light.<sup>16</sup> That the wavelength dependence does not simply follow the absorptivity of the silver halides however, requires a careful more systematic study using two lasers in order to eliminate effects due to the response of the sites to the incident light that yields the Raman spectrum. Also, any future experiments of the SERS excitation profile for electrochemical interfaces will have to take careful account of the light and dark ORC effect.

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## FIGURE CAPTIONS

Figure 1. Single scans of the SERS spectra of an Ag electrode immersed in 0.1M NaCl+0.01M NaSCN at -100 mV. A. Spectrum before performing an oxidation-reduction cycle (ORC). B. Spectrum recorded after an ORC in the dark, i.e., without laser illumination of the electrode. C. Spectrum recorded after an ORC with the laser continuously illuminating the electrode. Laser:  $\lambda_L = 530.9$  nm, 200 mW, p-polarized. ORC: double potential step from -100 mV to 250 mV and back to -100 mV after passage of 20 mC cm<sup>-2</sup> of anodic charge.

Figure 2. Evolution of SERS spectrum for the C-N stretching mode ( $\nu_{CN}$ ) of thiocyanate following the application of five consecutive double potential step ORC's. A. Spectra recorded immediately following the ORC's performed in the dark, c.f., Fig. 1B. B. Spectra recorded immediately after ORC's performed with the laser continuously irradiating the electrode, c.f., Fig. 1C. Laser and ORC parameters are the same as in Fig. 1. Spectra were recorded with an optical multichannel analyser. Each spectrum, 1848 to 2330 cm<sup>-1</sup>, recorded with an accumulation time of 2 s. Note that the low frequency side of each trace is on the right hand side.

Figure 3. SERS spectra for the metal-ligand stretching mode  $\nu_{ML}$  for an Ag electrode immersed in 0.1M NaCl solution. A. Recorded after an ORC performed in the dark. B. Recorded after an ORC performed with the laser illuminating the electrode continuously. Laser  $\lambda_L = 530.9$  nm, 200 mW, p-polarized. ORC parameters are the same as in Fig. 1.

Figure 4. SERS spectra for metal-ligand stretching mode  $\nu_{ML}$  for Ag electrode in contact with 0.1M NaCl solution. A. Spectrum after ORC performed in the dark. B. Spectrum after ORC with continuous irradiation of electrode with laser. ORC parameters are the same as in Fig. 1. Laser:  $\lambda_L=647.1$  nm, 600 mW, p-polarized.









